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(54) TABLETS CONTAINING BLEACHING ACTIVATORS, SUITABLE FOR USE WITH TEXTILE WASHING AGENTS

(71) We, HENKEL & CIE. GMBH a German Company, of 67 Henkelstrasse, Duesseldorf-Holthausen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to tablets containing bleaching activators, suitable for use with textile washing agents.

Washing agents are known which contain so-called bleaching activators in addition to the conventional cleansing washing active substances, builder salts and bleaching percompounds. These activators are carboxylic acid derivatives which react with the percompounds to form peracids and thus increase the bleaching effect of the mixtures or enable bleaching to be effected at relatively low washing temperatures. However, the storing of such washing agents gives rise to considerable problems, since the percompounds and bleaching activators can react with each other at room temperature under the influence of high atmospheric humidity, thus leading to a loss of active oxygen. If oxygen-sensitive substances are added, such as optical brighteners, they can be destroyed oxidatively. An unpleasant odour, attributable to the volatile products of oxidation, frequently occurs. Trouble can also occur in washing agents in which the percompounds are provided with coating substances or which are stored separately from the other constituents of the washing agent in order to prevent interaction with the other constituents. Since the bleaching activators constitute very reactive acylation agents, they can react with sensitive washing agent constituents, such as perfumes or optical brighteners, and impair the properties of the latter.

It has already been proposed to provide the powder particles, comprising the bleaching activator, with a coating in order to prevent interaction with the activator and the percompounds. The recommended coating agents were, for example, water-soluble, high-molecular compounds such as polyglycols, polyvinyl alcohol or cellulose ether, or water-insoluble substances such as fatty acid or fatty alcohols which are sprayed or granulated onto the activator. However, it has been found that these water-soluble compounds do not lead to any appreciable improvement in the storage property. Although the known insoluble coating agents effect a slight improvement in the storage property, the rate at which the coated particles dissolve in cold or lukewarm water is too low. Consequently, when used in automatic washing machines, a portion of the agents remain undissolved in the rinsing devices or do not dissolve with sufficient rapidity in the lukewarm liquor, so that the bleaching effect is inadequate in the particularly important range of from 40° to 60°C.

Furthermore, the consumer might desire to use a composite bleaching washing agent both for easily washable textiles, i.e. textiles to be washed at 40° to 60°C, and for articles which have to be boiled. The pre-requisite for this is that the washing agent should have good bleaching properties in the low and high ranges of temperature. However, the conventional washing agents do not entirely fulfil this pre-requisite.

These disadvantages are avoided, or a considerable improvement is achieved, by virtue of the present invention. Accordingly the invention provides a tablet suitable for use in textile washing agents containing perhydrates, which comprises 85 to 98 percent by weight of at least one granular bleaching activator which forms peracids with hydrogen peroxide and whose activation value, determined by the titration method as hereinafter defined, is at least 3, 0.2 to 5 percent by weight of a water-soluble, film-forming polymer with which the granules of the bleaching activator are coated, 1.6 to 15 percent by weight of a water-soluble or swellable starch in granular form and/or carboxymethyl starch, in granular form, and 0.2 to 1.5 percent by weight of a magnesium- and/or a calcium salt of a saturated fatty acid containing 16 to 20 carbon atoms.

Suitable tablets have a diameter of 5 to 50

mm and a thickness of 2 to 25 mm.

Suitable bleaching activators which form organic peracids with hydrogen peroxide or perhydrates in aqueous solution are, for example, N-acyl-, O-acyl compounds, carbonic acid- or pyrocarbonic acid ester, whose activation value for the percompounds (=titre) is at least 3, preferably at least 4.5. This activation value is determined by the following titration method:

Solutions which contain 0.615 g/l $NaBO_2 . H_2O_2 . 3H_2O$ (4 mMol/l) and 2.5 g/l $Na_4P_2O_7 . 10H_2O$ are heated to 60°C. 4 mMol/l activator are then added to the solutions which are then kept at the stated temperature for 5 minutes under agitation. 100 ml of this liquid is then poured onto a mixture of 250 g of ice and 15 ml of glacial acetic acid and is titrated immediately after adding 0.35 g potassium iodide with 0.1 N sodium thiosulphate solution and starch as an indicator. The quantity of thiosulphate solution consumed in ml is the activation value (=titre). It would be 8.0 ml with 100% activation of the peroxide used.

Among the types of activators still to be described below, those compounds having a melting point of at least 70°C, preferably at least 100°C, and particularly at least 150°C, are particularly suitable. Furthermore, the equivalent weight of these compounds is preferably no more than 170, especially no more than 130, and particularly no more than 110 (in the present instance, "equivalent weight" refers to the quotient from the molecular weight and the number of acyl radicals or carbonic acid radicals or pyrocarbonic acid radicals present in the molecular). The activators usable in accordance with the invention include:

a) N - diacylated and N,N′ - tetraacylated amines such as N,N,N′,N′ - tetraacetylmethylenediamine or -ethylenediamine, N,N - diacetylaniline and N,N - diacetyl - p - toluidine or 1,3 - diacylated hydantoins such as the compounds, 1,3-diacetyl - 5,5 - dimethylhydantoin and 1,3 - dipropionyl - hydantoin;

b) N - alkyl - N - sulphonyl - carbonamides such as the compounds N-methyl - N - mesyl - acetamide, N-methyl - N - mesyl - benzamide, N-methyl - N - mesyl - p - nitrobenzamide, and N - methyl - N - mesyl - p - methoxybenzamide;

c) N - acylated cyclic hydrazides, acylated triazoles or urazols such as monoacetyl maleic acid hydrazide;

d) O,N,N, - trisubstituted hydroxylamines such as O-benzoyl - N,N - succinylhydroxylamine, O - acetyl - N,N-succinyl - hydroxylamine, O - p - methoxy - benzoyl - N,N - succinylhydroxylamine, O - p - nitro - benzoyl-N,N - succinyl - hydroxylamine and O,N,N - triacetyl - hydroxylamine;

e) N,N′ - diacetyl - sulphurylamides such as N,N′ - dimethyl - N,N′ - diacetylsulphurylamide and N,N′ - diethyl-N,N′ - dipropionyl - sulphurylamide;

f) Triacylcyanurates such as triacetylcyanurate and tribenzoylcyanurate;

g) Carboxylic acid anhydrides such as benzoic acid anhydride, m - chlorobenzoic acid anhydride, phthalic acid anhydride, 4 - chlorophthalic acid anhydride;

h) sugar ester such as glucosepentaacetate;

i) 1,3 - diacyl - 4,5 - diacyloxy - imidazolidines such as the compounds 1,3-diformyl - 4,5 - diacetoxy - imidazolidine, 1,3 - diacetyl - 4,5 - diacetoxy - imidazolidine, 1,3 - diacetyl-4,5 - dipropionyloxy - imidazolidine;

j) tetraacetylglycoluril and tetrapropionylglycoluril;

k) diacylated 2,5 - diketopiperazines such as 1,4 - diacetyl - 2,5 - diketopiperazine, 1,4 - dipropionyl - 2,5 - diketopiperazine, 1,4 - dipropionyl - 3,6-dimethyl - 2,5 - diketopiperazine;

l) acylation products of propylene diurea or 2,2 - dimethyl - propylene diurea (2,4,6,8 - tetraaza - bycyclo - (3,3,1)-nonane - 3,7 - dione or its 9,9 - dimethyl derivate), particularly tetraacetyl- or tetrapropionyl - propylene diurea or its dimethyl derivates;

m) carbonic acid ester such as sodium salts of p - (ethoxycarbonyloxy) - benzoic acid and p - (propoxycarbonyloxy)-benzene sulphonic acid.

The types of activator mentioned under a) and g) are of particular interest. Preferably, tetraacetylglycoluril is used in quantities of from 90 to 97 percent by weight.

The bleaching activators should be present in granular form, particularly in the form of granules having an average diameter of from 0.05 to 2 mm, preferably from 0.1 to 1 mm. The granules are provided with a coating of water-soluble, film-forming polymers. Suitable polymers are carboxymethyl cellulose and carboxymethyl starch, methyl- or hydroxyethyl cellulose, gelatines, alginates, polyethylene glycol, polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylates and polymethacrylates, the polymers containing carboxyl groups preferably being present in the form of sodium salts. Alternatively, mixtures of polymers may be used. The quantity of film-forming polymers should be 0.2 to 5 percent by weight, preferably 0.3 to 2 percent by weight, relative to the total weight of the tablets. Preferred polymers are carboxymethyl cellulose in quantities of up to 1 percent by weight based on the total weight of the tablet, or polyvinyl alcohol in

quantities of up to 2 percent by weight based on the total weight of the tablet.

The starch contained in the tablets is water-soluble or swellable and can be a native starch such as potato, maize, wheat or rice starch, or starch preparations which have been partially chemically peptized, or chemically modified by carboxymethylation. Particularly suitable starches are native potato starch and carboxymethyl starch which has 0.15 to 0.5 carboxymethyl groups per unit of anhydroglucose. Alternatively, a starch preparation may be used which is commercially available under the Registered Trade Mark "Noredux" and which may be produced by thermal reduction of a natural starch, such as potato, maize or wheat starch, in vacuo in the presence of small quantities of acid and, if required, subsequent interlacing with small quantities of formaldehyde, and which has a viscosity of 3000 to 6000 cP, preferably 4000 to 5000 cP in a 5% aqueous solution at 20°C. It is also possible to use mixtures of the above-mentioned starches and starch preparations, particularly mixtures of carboxymethyl starch and potato starch.

Suitable lubricants present in quantities of from 0.2 to 1.5, preferably from 0.4 to 1 percent by weight, are primarily calcium- and magnesium stearate, also the corresponding palmitates and arachinates and mixtures thereof with stearates.

To improve the tablet-forming property and the decomposing properties, the mixtures may also contain mineral, finely powdered adsorption agents, particularly fine-particulate or colloidal silicon dioxide (Aerosil®), calcium hydrogen phosphate, calcium, carbonate, magnesium oxide, magnesium silicate, aluminium oxide and aluminosilicate. Their quantities can be 1.5, preferably 0.2 to 0.8, percent by weight. Adhesion can be prevented by coating the pressing tool with polymers containing fluorine, such as teflon®.

To improve the dissolving power, the tablets can contain up to 2 percent by weight of a wetting agent, such as sodium lauryl sulphate, sodium dioctyl sulphonsuccinate, sodium alkylsulphonate, having 10 to 15 carbon atoms, sodium alkyl naphthalene sulphonates or other surface-active substances such as are given hereinafter as constituents of the washing agent. Furthermore, dyes or pigments can be present in order to give the tablets a conspicuous colour such as a speckled colour, or a physiologically harmless substance having an unpleasant taste, in order to prevent anyone eating the tablets by mistake.

The tablets are manufactured by previously granulating the bleaching activators by using conventional granulating and spray-mixing devices with an aqueous solution of the aforementioned water-soluble polymers, the particles being provided with a film-like coating comprising the polymeric material. Solutions having a polymer content of from 1 to 5 percent by weight and a viscosity of no more than 7000 cP have proved to be suitable. Suitable devices are, for example, granulating drums or mixing devices equipped with agitator elements or operating on the fluid bed principle. Surplus water is removed from the particles, for example by introducing heated air, or by subsequent after-drying. The granulated materials are subsequently mixed with the other constituents of the tablets and pressed at a pressure of 100 to 1000 kg/cm². Advantageously, the tablets have a diameter of 10 to 30 mm and a thickness of 3 to 20 mm, since tablets of this size are convenient to handle and decompose with sufficient rapidity in cold water.

The composition of the tablets is so chosen that the tablets are sufficiently stable, although having a relatively short decomposing time of 30 to 60 seconds in water at room temperature. This property is of special importance, since the rinsing time and the quantity of water introduced into the rinsing device are limited in the conventional fully automatic washing machines. The tablets and the metered supply of washing agent dissolve in substantially the same period of time. This prevents the textile material, still in the dry state in the washing drum, from coming into contact with solutions of different concentrations of washing agent and activator in the region of the inlet, which might lead to non-uniform bleaching results.

The tablets may be packaged by sealing them in a metal or plastics material film and placing them into the package filled with washing agent, or attaching them to the outside of the package. In the latter case, the package is preferably provided with appropriate depressions for receiving the tablets.

The main constituents of the washing agents, with which the tablets are combined in the above-mentioned manner, are surface-active crude washing materials, at least one builder salt from the class of the polyphosphates, washing alkalis and sequestering agents, percompounds and further conventional washing aids and additives. The agents can be present in liquid, pulverulent, granular or lumpy form.

The tablets in accordance with the invention, or their combination with washing agents containing perhydrates, have considerable advantages compared with conventional washing agents. In particular, it may be emphasized that, even when stored under comparatively unfavourable conditions, there is no loss of active oxygen and activating agents, and no decomposition of sensitive constituents of the washing agent. Furthermore, the consumer has the possibility of optionally varying the bleaching effect by appropriate metering of the activator and thus adapting it to the type of textile or degree of soiling with-

out the risk of damaging the textiles by unsuitable temperatures of the washing bath. When using tetraacetylglycoluril, 3 to 15 g of bleaching activator is normally required in a washing operation with 4 to 5 kg of dry washing, a quantity which may be conveniently accommodated in 1 to 5 tablets.

EXAMPLES

Examples 1 and 2

93.5 parts by weight of tetraacetylglycoluril were sprayed with 0.5 parts by weight of a sodium carboxymethyl cellulose, dissolved in 25 parts by weight of water, in a fluid bed mixer (Example 1) in which the mixture to be granulated was held in suspension by means of air of 70°C and thoroughly mixed, or in a rolling drum mixer (Example 2). The carboxymethyl cellulose had a degree of substitution of 0.5 carboxymethyl groups per unit of anhydroglucose. The granulated substance produced in the fluid bed mixer was cooled to room temperature by blowing air into the mixer, while the granulated substance removed from the drum mixture was spread out on racks and subjected to a final drying process in a drying cabinet at 50°C. The granulated substances had the following screen numbers and weight per litre:

Example		
Mesh size	1	2
>0.8 mm	—	4.6%
>0.4 mm	8.6%	30.8%
>0.2 mm	36.6%	36.7%
>0.1 mm	39.8%	21.4%
<0.1 mm	14.7%	6.4%
weight per litre	620 g	560 g

The granulated substances were mixed with 2.2 parts by weight of a sodium carboxymethyl starch (potato starch with 0.25 carboxymethyl groups per unit of anhydroglucose, water content approximately 10%), 3 parts by weight of native potato starch and 0.8 parts by weight of magnesium stearate and pressed with a pressure of approximately 400 kg/cm² to form tablets having a diameter of 20 mm, a thickness of 9 mm, and a weight of 3.3 g.

In order to check the rate of decomposition, the tablets were thrown into a glass beaker having a capacity of 400 ml and filled with 200 ml of water of 18°C and 16° German hardness. After a rest period of 10 seconds, agitation was effected at 500 r.p.m. by means of a magnetic agitator (the stirring rod was coated with Teflon® and was 30 mm long and 7 mm thick). The tablets had completely decomposed 35 to 40 seconds after the commencement of the test (25 to 30 seconds after the agitator was put in operation), and the components had been dissolved or dispersed within 40 seconds.

Example 3

In a similar manner to that described above, 94.1 parts by weight of tetraacetylglycoluril with 0.5 parts by weight of sodium carboxymethyl cellulose (degree of substitution 0.5) in a 2% aqueous solution were granulated in a mixing container (Lödige mixer) equipped with stirring paddles. The granulated substance obtained, dried with hot air, had the following screen numbers with a weight per litre of 550 g:

>0.8 mm 8.0%, >0.4 mm 35.6%, >0.2 mm 25.8%, >0.1 mm 24.3%, <0.1 mm 6.2%,

The granulated substance was pressed with 4.2 parts by weight of Na - carboxymethyl starch (substitution degree 0.25), 0.6 parts by weight of magnesium stearate and 0.6 parts by weight of Aerosil to form tablets having a diameter of 30 mm, a thickness of 8.5 mm, and a weight of 3.0 g. The dissolving test, carried out in accordance with Examples 1 and 2, resulted in a decomposition time of 30 to 35 seconds.

Example 4

95.5 parts by weight of tetraacetylglycoluril were sprayed with a solution of 1 part by weight of polyvinyl alcohol (polermerisation degree 2000) and 20 parts by weight of water and granulated at 70°C in a fluid bed mixer in accordance with Example 1. The granulated substance had a weight per litre of 550 g and resulted in the following screen numbers:

>0.8 mm 0%, >0.4 mm 5.8%, >0.2 mm 39.5%, >0.1 mm 45.8%, <0.8 mm 8.6%

After mixing with 2.6 parts by weight of Na-carboxymethyl starch (substitution degree 0.23) and 0.9 parts by weight of magnesium stearate, tablets were manufactured which had a diameter of 20 mm, a thickness of 9 mm, and a weight of 3.0 g and which, in the decomposition test given in Example 1, had a decomposition time of 30 seconds.

Example 5

90 parts by weight of tetraacetylglycoluril were sprayed with 3 parts by weight of a polyglycol (average molecular weight 9000) in 15 parts by weight of water in a granulating drum at 50°C and granulated. Particles having a diameter of from 0.1 to 0.8 mm constituted 95% of the granulated substance. This preliminary mixture was mixed with further additives and pressed to form tablets of 300 mm diameter and 8 mm thickness. The composition was as follows (in percents by weight):

90.0% tetraacetylglycoluril
3.0% polyethylene glycol
5.5% potato starch
0.5% sodium lauryl sulphate
0.5% Aerosil 200®
0.5% magnesium stearate

The decomposition time was 50 seconds.

Example 6

89 parts by weight of tetraacetylglycoluril were provided with a film-like coating of 1.5 parts by weight of gelatine in 30 parts of water in a granulating drum. The dried granulated substance was, as described in Example 5, pressed with further constituents to form tablets of the following composition (in percents by weight):

88.5% tetraacetylglycoluril
1.5% gelatine
8.0% potato starch
0.5% sodium lauryl sulphate
1.0% magnesium stearate
0.5% Aerosil 200[2]

The decomposition time was 50 seconds.

Tablets having similar properties are obtained if other activators such as tetraacetylmethylenediamine or tetraacetylethylenediamine are used instead of tetraacetylglycoluril.

WHAT WE CLAIM IS:—

1. A tablet suitable for use in textile washing agents containing perhydrates, which comprises 85 to 98 percent by weight of at least one granular bleaching activator which forms peracids with hydrogen peroxide and whose activation value determined by the titration method as hereinbefore defined is at least 3, 0.2 to 5 percent by weight of a water-soluble, film forming polymer with which the granules of the bleaching activator are coated, 1.6 to 15 percent by weight of a water soluble or swellable starch in granular form and/or carboxymethyl starch in granular form, and 0.2 to 1.5 percent by weight of a magnesium- and/or a calcium salt of a saturated fatty acid containing from 16 to 20 carbon atoms.

2. A tablet as claimed in claim 1, in which the activator comprises tetraacetylglycoluril.

3. A tablet as claimed in claim 1 or claim 2, in which the activator has an average grain size of from 0.1 to 1 mm.

4. A tablet as claimed in any one of claims 1 to 3, in which the film-forming polymer comprises sodium carboxymethyl cellulose in quantities of up to 1 percent by weight of the total weight of the tablet.

5. A tablet as claimed in any one of claims 1 to 3, in which the film-forming polymer comprises polyvinyl alcohol in quantities of up to 2 percent by weight of the total weight of the tablet.

6. A tablet as claimed in any one of claims 1 to 5, in which the starch comprises native potato starch.

7. A tablet as claimed in any one of claims 1 to 5, in which the carboxymethyl starch comprises sodium carboxymethyl starch having from 0.15 to 0.5 carboxymethyl groups per unit of anhydroglucose.

8. A tablet as claimed in any one of claims 1 to 7, having a content of from 0.4 to 1 percent by weight of magnesium stearate as the salt of a saturated fatty acid.

9. A tablet as claimed in any one of claims 1 to 8, having a content of up to 2 percent by weight of an adsorption agent which is a mineral.

10. A tablet as claimed in claim 9 having from 0.2 to 0.8 percent by weight of an adsorption agent which is a mineral.

11. A tablet as claimed in claim 9 or claim 10 in which the adsorption agent comprises fine-particuate silicon dioxide.

12. A tablet as claimed in any one of claims 1 to 11, having a content of up to 2 percent by weight of a surface-active wetting agent.

13. A tablet as claimed in any one of claims 1 to 12, in which the tablets have a diameter of from 5 to 50 mm and a thickness of from 2 to 25 mm.

14. A tablet as claimed in claim 13 in which the tablets have a diameter of from 10 to 39 mm, and a thickness of from 3 to 20 mm.

15. A tablet as claimed in claim 1 and substantially as hereinbefore described with reference to any one of the Examples.

W. P. THOMPSON & CO.,
Coopers Buildings,
12 Church Street,
Liverpool, L1 3AB.
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